SYNTHESIS AND MESOMORPHIC PROPERTIES OF SYMMETRIC AND NON-SYMMETRIC LIQUID CRYSTAL DIMERS CONTAINING METHYLENE AND DISULPHIDE SPACERS

by

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Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science

2012

ACKNOWLEDGEMENTS

I would like to express my greatest gratitude to my main supervisor, Professor Yeap Guan Yeow for his continuous support and encouragement during my master project. It has been a great pleasure and I really enjoyed working with him. Besides that, I am also grateful to Professor Yeap for giving me the golden opportunity to conduct part of my research in the University of Aberdeen, Scotland for a period of 3 months. I was extremely fortunate to benefit from the research attachment in numerous ways. My sincere and special thanks also go to my co-supervisor, Professor Wan Ahmad Kamil Mahmood for supporting the 3 months attachment in the University of Aberdeen and for giving me advice and assistance generously. I would like to thank my field-supervisor, Professor Corrie T. Imrie who has made his support available in a number of ways during my research attachment in the University of Aberdeen.

I am thankful to Professor Ewa Gorecka from Warsaw University, Poland and Associate Professor Daisuke Takeuchi from Tokyo Institute of Technology, Japan for their assistance in my sample analyses. I am also greatly indebted to Mr. Hng Tiang Chuan, Mr. Ong Chin Hin, Dr. Elham Altaifi, Dr. Lu Zi Bao and Dr. Peter A. Henderson for their inspiring guidance and unlimited encouragement throughout my research work. Likewise, I wish to show my appreciation to my laboratory mates for providing significant help during my research work.

Financial support from the Ministry of Higher Education (Malaysia), the Research University Grant Scheme (Universiti Sains Malaysia) and the Prime Minister Initiative Grant (British) are gratefully acknowledged.

Finally, I am very thankful to my beloved parents for their continuous support and love all this while.

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ABSTRAK

Empat siri dimer hablur cecair simetri and tak-simetri yang baru dengan pelbagai kumpulan berfungsi telah disintesis and dicirikan. Pencirian fizikal dan spektroskopi seperti analisis unsur (CHN), spektroskopi inframerah (FT-IR) dan spektroskopi resonans magnet nuklear (FT-NMR) telah dilakukan untuk mengenalpasti struktur molekul dimer ini. Kajian bagi kelakuan terma dan pemerhatian tekstur sebatian akhir telah dilakukan dengan menggunakan mikroskop terkutuban cahaya (POM) dan kalorimetri imbasan berbeza (DSC). Siri pertama dan kedua merupakan dimer tak-simetri, α-{4-[(4-tertukarganti-fenilimino)metil]-fenoksi}-ω-[4-(4-pentiloksikarbonilfenil)fenoksi]alkana yang terdiri daripada dua belas homolog yang berbeza dari segi spaser fleksibel (pentil dan heksil) dan kumpulan tertukarganti terminal (H, CH_3, C_2H_5, F, Cl, Br). Penyiasatan terhadap kelakuan terma menunjukkan bahawa dimer tanpa kumpulan tertukarganti adalah bukan mesogenik manakala sepuluh homolog yang selebihnya memaparkan fasa nematik yang dominan. Homolog yang mengandungi spaser pentil bernombor ganjil menunjukkan fasa nematik monotropik manakala homolog yang mengandungi spaser heksil bernombor genap menunjukkan fasa nematik enantiotropik. Tambahan lagi, homolog yang mengandungi atom bromin terminal dan spaser heksil juga memaparkan fasa smektik A dalam kitar penyejukan. Pengaruh saiz kumpulan tertukarganti terminal terhadap kestabilan sifat hablur cecair juga telah dikajikan. Sama seperti dimer ini, satu lagi siri dimer tak-simetri yang mengandungi atom iodin sebagai kumpulan tertukarganti terminal iaitu α-{4-[(4-iodofenilimino)metil]-fenoksi}-ω-[4-(4-pentiloksikarbonilfenil)fenoksi]alkana dengan spaser daripada

C_5H_{10} hingga $C_{12}H_{24}$ telah disediakan. Dimer yang mengandungi spaser C_6H_{12} dan C_7H_{14} memaparkan fasa nematik manakala dimer yang mengandungi spaser C_9H_{18} sehingga $C_{12}H_{24}$ memaparkan fasa smektik A. Sementara itu, dimer yang mengandungi spaser C_8H_{16} menunjukkan kedua-dua fasa nematik enantiotropik dan fasa smektik A monotropik. Kesan ganjil-genap yang nyata pada kedua-dua takat jelas dan takat lebur telah diperhatikan apabila panjang spaser diubah, di mana ahli yang mengandungi spaser genap memaparkan takat jelas yang lebih tinggi daripada ahli yang mengandungi spaser ganjil. Siri keempat iaitu dimer titian-disulfida, bis[ω-(kolesteriloksikarbonil)alkil] disulfida terdiri daripada unit berasaskan kolesterol dan dimer ini memaparkan fasa kiral nematik. Selain daripada fasa kiral nematik, fasa smektik A juga diperhatikan bagi homolog yang mengandungi spaser fleksibel yang lebih panjang. Eksperimen difraksi sinar-X mendedahkan struktur '*intercalated*' fasa smektik A bagi dimer ini. Kewujudan ikatan disulfida meningkatkan fleksibiliti spaser bagi dimer ini dan menyebabkan penurunan suhu peralihan kiral nematik-isotropik. Di samping itu, kesan ganjil-genap juga dirakamkan dalam siri dimer ini.

SYNTHESIS AND MESOMORPHIC PROPERTIES OF SYMMETRIC AND NON-SYMMETRIC LIQUID CRYSTAL DIMERS CONTAINING METHYLENE AND DISULPHIDE SPACERS

ABSTRACT

Four series of new symmetric and non-symmetric liquid crystal dimers with multi-functional groups have been synthesised and characterised. Physical and spectroscopic characterisations such as elemental analysis (CHN), infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (FT-NMR) have been carried out to elucidate the molecular structures of the dimers. The studies of thermal behaviour and texture observation of the final compounds are performed by means of polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The first and second series of non-symmetric dimers, α-{4-[(4-substituted-phenylimino)methyl]phenoxy}-ω-[4-(4-pentyloxycarbonylphenyl)phenoxy]alkanes consist of twelve homologues which vary in terms of flexible spacers (pentyl and hexyl) and terminal substituents (H, CH_3, C_2H_5, F, Cl, Br). Investigation on the thermal behaviour shows that the dimers without terminal substituent are not mesogenic while the remaining ten homologues exhibit the nematic phase predominantly. The homologues incorporated with odd-numbered pentyl spacers exhibit the monotropic nematic phase while homologues incorporating the even-numbered hexyl spacers show the enantiotropic nematic phase. Additionally, the homologue with a terminal bromine atom and a hexyl spacer also exhibit a smectic A phase during the cooling cycle. Influence of the terminal substituent size in stabilising the liquid crystalline properties is also studied. Analogous to these dimers, another series of non-symmetric dimers with iodine atom as terminal substituent namely α-{4-[(4-iodophenylimino)methyl]phenoxy}-ω-[4-(4-pentyloxycarbonylphe-nyl)phenoxy]alkanes with spacer ranging from C_5H_{10} to $C_{12}H_{24}$ have been prepared.

The dimers with C_6H_{12} and C_7H_{14} spacers exhibit the nematic phase while dimers consist of C_9H_{18} to $C_{12}H_{24}$ spacers exhibit the smectic A phase. On the other hand, dimer with C_8H_{16} spacer shows both enantiotropic nematic and monotropic smectic A phases. Strong odd-even effect in both clearing and melting temperatures is observed as the length of the spacer is varied, in which the members with even spacers exhibit higher clearing points than their counterparts possessing odd spacers. The fourth series of disulphide-bridged dimers, bis[ω-(cholesteryloxycarbonyl)alkyl] disulphides are composed of cholesterol-based units and these dimers exhibit the chiral nematic phase. Apart from the chiral nematic phase, the smectic A phase is also observed for homologues with longer flexible spacers. X-ray diffraction experiment reveals the intercalated structure of the smectic A phase of these dimers. The presence of disulphide bond increases the spacer flexibility of these dimers thus resulting in lower chiral nematic-isotropic transition temperatures. Besides that, odd-even effect is also recorded for this series of dimers.

1.0 INTRODUCTION

1.1 Liquid crystals (LC)

Liquid crystals (LC) are considered as the fourth state of matters following the three most common states of matters which are solids, liquids, and gases (Kumar, 2001). Generally, a transition between the different states is induced by a change in temperature. Water, for example, exist as a solid at temperature below 0 ^{o}C, as a liquid at temperature between 0 ^{o}C to 100 ^{o}C and as a gas at temperature above 100 ^{o}C. However, when heat is applied to a liquid crystal substance, another state of matters is observed in between the solid and the liquid phases which is called the liquid crystal phase. This is also why liquid crystal phases are also termed as mesophases. One or more mesophases could be observed in between the solid and liquid states depending on the chemical nature and the structure of the liquid crystal compounds. In order to further characterise these liquid crystal phases and transitions, we must first consider what, exactly, distinguishes phases of matter from one another.

The familiar phases of solid, liquid and gas differ from each other on an apparent manner: a crystalline solid is to large extent rigid and not compressible, a liquid is able to flow and take the shape of its container but is not very compressible while a gas is both fluid and compressible. These macroscopic differences stem from microscopic differences in the way the molecules arrangement themselves in each phase, and these differences can be described using the concept of order.

In a crystalline solid phase, the molecules are well arranged and are rigidly bound together both in space and orientation. Once the position of a molecule and its neighbouring molecules are known at one point, the place of each molecule is known precisely over the crystal lattice. This means that a given molecule will more or less remain in a certain position and in the crystal lattice, and remain pointed in certain

direction. Therefore molecules in a solid possess a high degree of positional order and also a high degree of orientational order.

On the other hand, molecules in the liquid phase are randomly positioned. There is no fixed position of molecules relative to each other and molecules are able to move freely. Besides that, the molecules also lack any preferred orientation. This makes the phase isotropic and thus a liquid phase can also be termed an isotropic phase in the field of liquid crystal studies. Therefore it is plausible to say that molecules in the isotropic liquid phase have almost no positional or orientational order.

In the liquid crystal phases, the molecules possess an intermediate amount of order between that of the crystalline solid and isotropic liquid phases. The simplest liquid crystal phase is known as the nematic (N) phase. The N phase has no long-range positional order of the centre mass of the molecules wherein the molecules are able to flow pass each other but the long axes of the molecules tend to line up pointing in a preferred direction specified by the unit vector, *n*, known as the director (Andereck, 1995). Nevertheless, the phase is recognisable as nematic by the formation of droplets at the transition point, by the dim flash, and by the high mobility of the phase (Henderson *et al.*, 2001). Hence, the N phase is a phase with very little positional order, like the isotropic liquid phase, but some amount of orientational order. Another type of LC phase that is commonly observed in liquid crystalline materials is the smectic phases. The smectic A (SmA) phase is the simplest smectic phase among the Sm phases in which the molecules not only tend to point along a director, but also tend to organise themselves into layers (Collings, 1990). Thus there is orientational order like in the N phase, and additionally a small amount of positional orders. Specifically for the SmA phase, the molecules are

arranged, in average, perpendicularly to the layers (Kumar, 2001). As a phase with higher order than the N phase, the smectic phase therefore occurs at lower temperature than the N phase (Andereck, 1995). The SmA phase is identified on the basis of its fan-like textures as reported previously for many types of liquid crystals including symmetric dimeric liquid crystals reported by Weissflog *et al.* (1999). Figure 1.1 shows a schematic depiction of the molecular arrangement in each of the four phases (crystalline solid, SmA, N, and isotropic liquid) mentioned above. It is important to note that the isotropic and the N phases have very low positional order or almost none but the N phase has considerably less orientational order than the SmA and crystalline phases, but more than the isotropic phase. On the other hand, molecules in the SmA phase behave in a very similar manner to those in the solid phase but with more rotation and translational freedom.

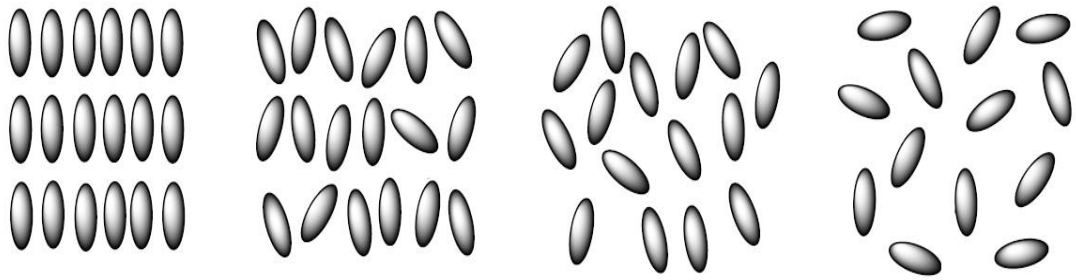


Figure 1.1. Schematic depiction of the crystalline (solid), smectic A, nematic and isotropic (liquid) phases

It should be noted at this point that besides the four phases discussed above, there are more phases that liquid crystalline materials can exhibit. As an example, besides the SmA phase, there are also a variety of other smectic phases such as SmB, SmC, SmE and more. On top of that, the N and Sm phases may additionally be chiral in which the director undergoes some kind of periodic rotation throughout the sample.

For the purposes of this thesis, however, only phases of concern will be discussed such as the N, chiral nematic (N*) or cholesteric and SmA phases. The chiral nematic phase composed of chiral molecules, or induced by the presence of chiral molecules (Robinson *et al.*, 2005). It is also called the cholesteric phase because it was first observed for cholesterol derivative (Dierking, 2003 and Kumar, 2001). There are some sort of intermolecular interactions that exist between the molecules' chiral centres that favour alignment at a slight angle between neighbouring molecules. These interactions result in a structure of thin twisted layer that can be visualised as a helical ordering perpendicular to the long axis of the molecules (de Vries, 1951). Interestingly, the helix may be right- or left-handed depending on the molecular chirality. The pitch, *p*, refers to the distance over which the LC molecules undergo a full 360^{o} twist and this resulted in a unique property of this phase wherein light with a wavelength equal to the pitch will be selectively reflected and circularly polarised (Singh, 2002 and Kumar, 2001). This behaviour has resulted in some unique optical properties exhibited by the cholesteric phase such as Bragg reflection and low-threshold laser emission which are exploited in various kinds of optical applications (Dierking, 2003 and Sluckin *et al.*, 2004). Figure 1.2 depicts the schematic representation of the cholesteric phase. Typical textures exhibited by the cholesteric phase are the oily streak texture and the fingerprint texture (Dierking, 2003).

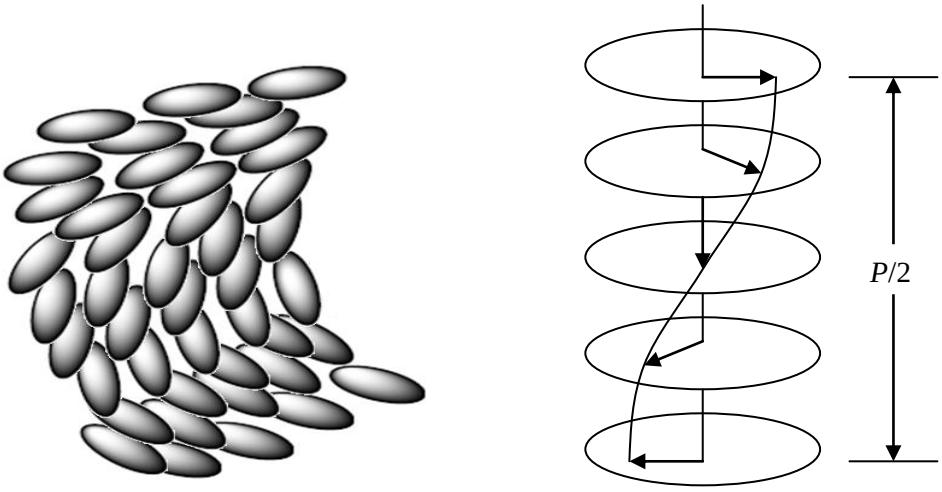


Figure 1.2. Schematic depiction of the cholesteric phase (N*) and the chiral pitch, *p* (Madhusudana, 2001)

1.2 Molecular structure and their LC phases

Molecules that exhibit liquid crystalline properties are usually anisotropic in shape and their liquid crystalline properties depend on non-covalent interactions. Several different types of shapes and their corresponding LC phases can be distinguished. According to previous findings, there are some general tendencies for certain types of molecules to exhibit distinct mesophases. However, it should be noted that the prediction of the kind of mesophase based solely on the molecular shape is not always possible.

1.2.1 Rod-shaped mesogens

The most common type of liquid crystals is those that consist of rod-like geometrical shape molecules (also known as calamitic molecules). These calamitic mesogens usually consist of two or more central ring systems which are known as the rigid core together with one or two flexible alkyl tails (Gray, 1979). The general templates used to describe the structure of calamitic mesogens are illustrated in Figure 1.3.

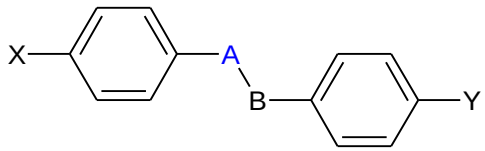
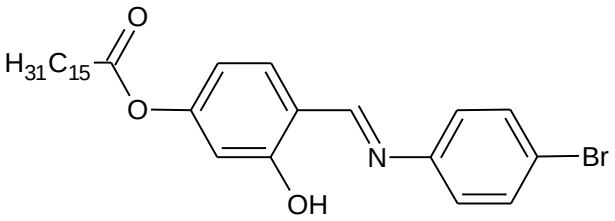
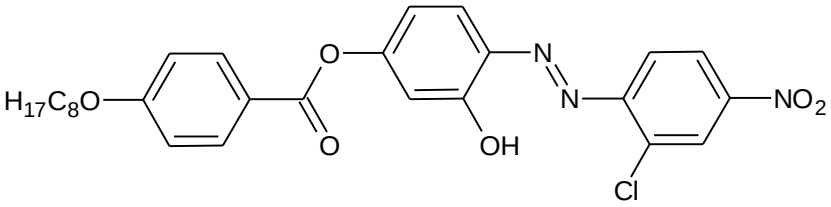


Figure 1.3. General structure of a calamitic mesogen

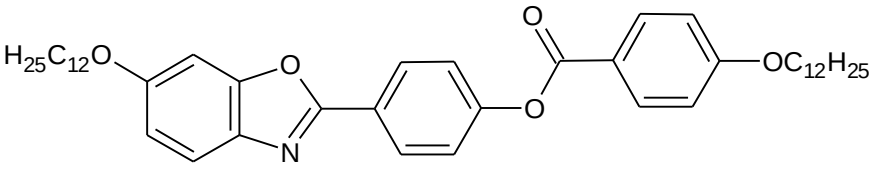
The two aromatic rings act as the rigid core which gives rise to the rigidity of the molecules that enables the molecules to arrange themselves in certain manner. Besides aromatic rings, heteroaromatic rings can also be used as the core units and these rings can be connected directly to one another or connected by the linking groups A and B. Some of the common linking groups used in liquid crystalline molecules include the azomethine, ester, thioester, azo groups and more. On the other hand, the X and Y represent the terminal groups. Usually, at least one of the terminal groups is linked to an alkyl chain in order to give rise to the flexibility of the molecules which is essential for the formation of liquid crystal mesophases. Other types of terminal groups commonly seen in liquid crystalline compounds are polar substituent such as the CN, NO_2 or the halogens. Table 1.1 shows examples of the central linking groups and the terminal groups. Some examples of calamitic liquid crystals molecules containing different mesogenic cores, central linking groups and terminal groups are depicted in Figure 1.4.



(a)



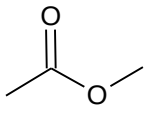
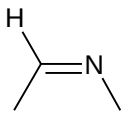
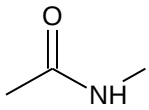
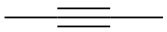
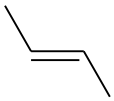
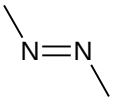
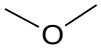
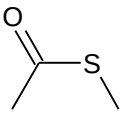
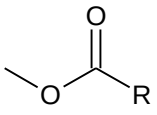
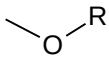
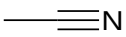
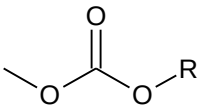
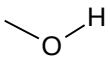
(b)



(c)

Figure 1.4. (a) *o*-Hydroxy-*p*-n-hexadecanoyloxybenzylidene-*p*-bromoaniline (Yeap *et al.*, 2004), (b) 2-chloro-4-nitro-2'-hydroxy-4'-(4''-n-octyloxybenzoyloxy)-azobenzene (Prajapati *et al.*, 2008), (c) 4-dodecyloxybenzoic acid 4-(6-dodecyloxy-benzoxazol-2-yl)phenyl ester (Chung *et al.*, 2005)

Table 1.1. Examples of central linking groups and terminal groups

Central linking groups (A and B)	Terminal groups (X and Y)
       	 H   —R F, Cl, Br, I   *R = C_nH_{2n+1}

1.2.2 Disc-shaped mesogens

Disc-shaped liquid crystals which are also known as discotic liquid crystals usually consist of relatively flat disc-shaped core with long pendant flexible chain substituents, commonly with ester or ether as the linking groups. Discotic liquid crystals exhibit columnar phase wherein stacks of disc-like molecules are present (Bushby and Lozman, 2002). Several kinds of columnar mesophases can be formed as a result of different molecular arrangements within the columns. On top of that, the columns can be tilted or non-titled and they can be arranged in a hexagonal or rectangular manner. Besides the columnar phases, disc-like molecules can also form lower ordered nematic phases of which several variants are known (Tinh *et al.*, 1979 and Praefcke *et al.*, 1991). Recently, a smectic-like (lamellar) phase has also been

reported but the precise arrangement of the molecules in each layer in not yet fully understood. A typical discotic molecule is shown in Figure 1.5.

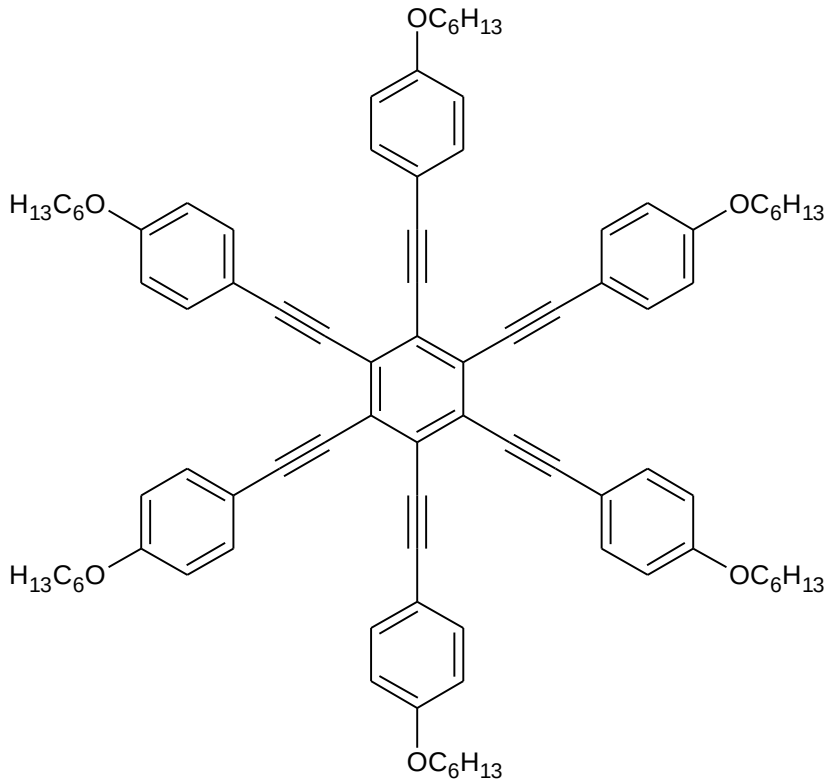
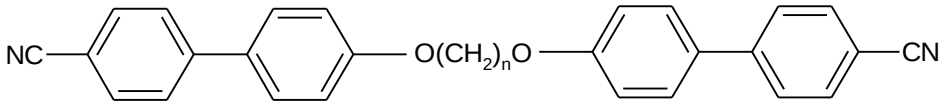


Figure 1.5. A discotic mesogen (Kohne and Praefcke, 1984)

1.2.3 Dimeric mesogens

In typical liquid crystal dimers or dimeric mesogens, two mesogenic entities are connected via a flexible central spacer (Luckhurst, 1995). Liquid crystal dimers can be divided into two broad classes: symmetric and non-symmetric (Barón, 2001, Marcelis *et al.*, 1995, Attard *et al.*, 1994). Symmetrical dimesogens in which the two mesogenic units are identical have been studied extensively. The most extensively studied series of symmetric liquid crystal dimers is depicted in Figure 1.6.



n = 3-12

Figure 1.6. α,ω-Bis(4-cyanobiphenyl-4'-yloxy)alkanes (Emsley *et al.*, 1984)

Interestingly for symmetric dimers, a simple empirical relationship relating the occurrence of smectic behaviour to the molecular structure was deduced from studies on the α,ω-bis(4-*n*-alkyl-anilinebenzylidene-4'-oxy)alkane series. Specifically, to obtain smectic properties the terminal chain length much be greater than half the spacer length, in the other cases nematic behaviour was observed (Date *et al.*, 1992). In addition to that, X-ray diffraction studies showed that all the smectic phases possessed a monolayer structure wherein the layer spacing is almost similar to the molecular length. This simple monolayer structure is thought to be stabilized by the microphase segregation into three regions as shown in Figure 1.7(a).

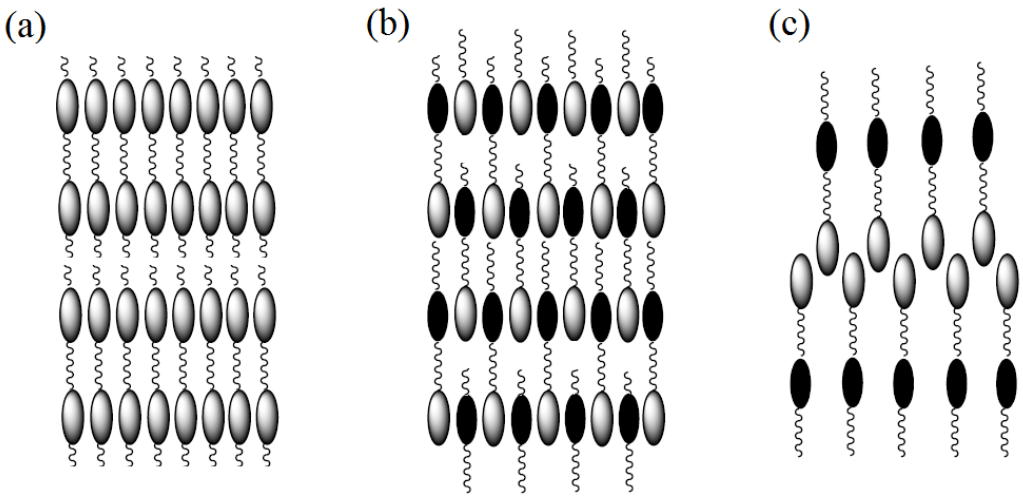


Figure 1.7. Schematic representation of SmA arrangements of liquid crystal dimer: (a) Monolayer, (b) intercalated and (c) interdigitated (Imrie and Henderson, 2007)

Dimesogenic compounds consisting of two different mesogenic units interlinked through a central spacer are known as non-symmetric dimers (Attard *et al.*, 1994). An example of previously reported non-symmetric liquid crystal dimer is shown in Figure 1.8. Although this class of liquid crystals has also been described in literature, they are considered as a relatively new class of liquid crystalline compounds that still require more research in order to establish their structure-property relationship.

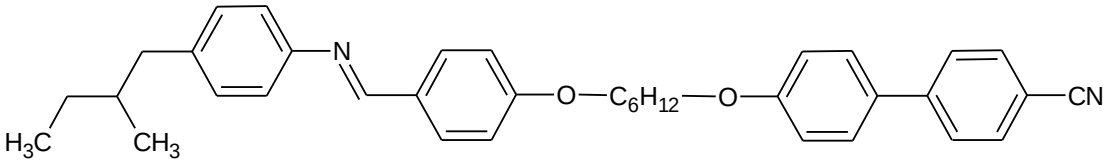


Figure 1.8. (S)-α-(4'-cyanobiphenyl-4-yloxy)-ω-{4-[4-(2-methylbutyl)phenylimino-methyl]phenoxy}hexane (Blatch *et al.*, 1997)

One of the interesting findings in which some non-symmetric dimers exhibit various modification within the smectic phases such as the intercalated and interdigitated phases shown in Figures 1.7(b) and 1.7(c) has made non-symmetric dimers the focus of recent research (Imrie and Henderson, 2002). These unconventional smectic phases result from the predominant intermolecular forces that exist between the two unlike mesogenic cores. As such, these forces stabilise the intercalated and interdigitated arrangement among molecules resulting in molecular arrangement which is entropically more favourable. This type of arrangement is rarely observed in dimers with symmetric architecture.

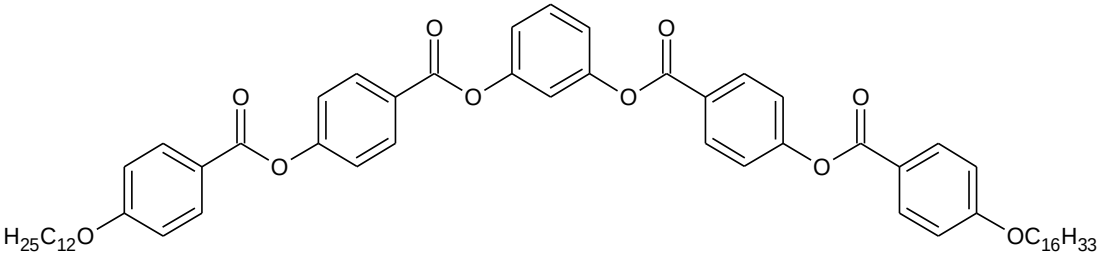
Liquid crystals dimers has received considerable attraction in recent years owing to their role as model compounds for the understanding of the technologically important semi-flexible main chain liquid crystal polymers and later as model compounds for side group liquid crystal polymers (Luckhurst, 1995 and Imrie *et al.*, 1993). The most striking similarity between the dimers and semi-flexible polymers is the dramatic dependence of the transition temperatures and the entropy changes on the length and parity of the flexible spacer which is known as the odd-even effect (Griffin and Britt, 1981).

Other examples of recent studies on this class of materials include investigation of the role of the spacer in determining the liquid crystal behaviour (Yeap *et al.*, 2009 and Imrie *et al.*, 1998), laterally connected dimers (Yoshizawa *et al.*, 2005 and Yoshizawa *et al.*, 2006), bent core dimers (So *et al.*, 2009), cholesteryl-containing dimers (Majumdar *et al.*, 2009 and Do *et al.*, 2006), hydrogen-bonded dimers (Tian *et al.*, 1997), the light emitting and flexoelectric properties of dimers (Kraft *et al.*, 1998, Aziz *et al.*, 2008, Srivastava *et al.*, 2008).

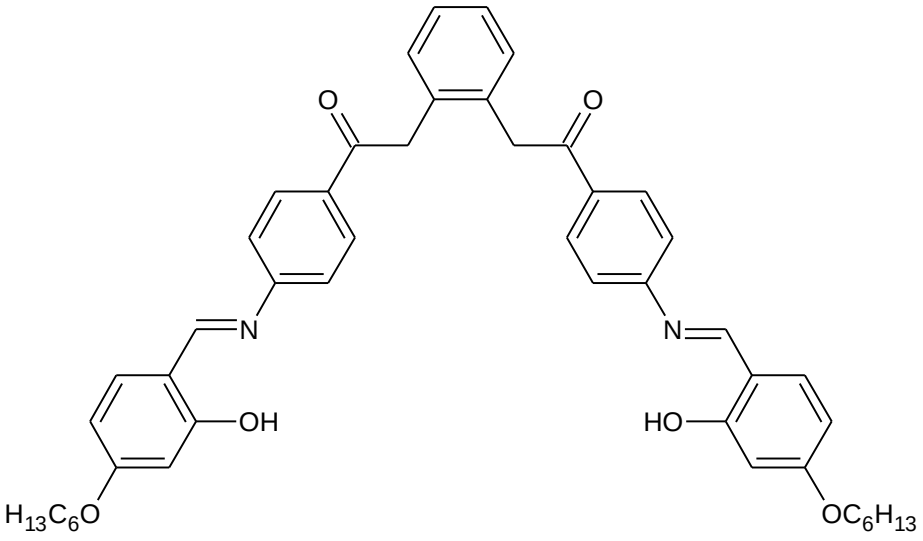
1.2.4 Non-conventionally-shaped mesogens

Non-conventionally-shaped liquid crystals are molecules with an anisotropic shape that deviates from the classical disc- and rod-shaped molecules (Tschierske, 1998). Some of these molecules namely banana-shaped or bent-core mesogens exhibit quite unusual mesophases morphologies and have therefore emerged as a new sub-field in the liquid crystal area. The ability of these molecules to exhibit astonishing liquid crystalline phases and (anti)ferroelectricity properties which was once thought to be exclusive for the chiral molecules has made bent-core mesogens the focus of current research (Pelzl, 1999). Generally, banana-shaped mesogens are

constituted of two mesogenic groups linked through a bent central core via linking groups and two flexible tails at both ends (Barón, 2001). Some examples of bent rigid groups are the 1,3-disubstituted benzene, 2,7-disubstituted naphthalene (Amaranatha Reddy and Sadashiva, 2000), 2,5-disubstituted 1,3,4-oxadiazol and the 2,5-disubstituted-thiophene (Dingemans and Samulski, 2000). An example of banana-shaped mesogen is depicted in Figure 1.9(a).



(a)



(b)

Figure 1.9. Structures of (a) banana-shaped mesogen (Achten, 2004) and (b) V-shaped mesogen (Yelamaggad *et al.*, 2004)

V-shaped mesogens possess structures that are almost similar to banana-shaped compounds. The only difference is that in contrast to banana-shaped mesogens, the two mesogenic units are substituted at the 1,2-position of the benzene ring (Attard and Douglass, 1997). Despite the similarity in shape, V-shaped mesogens usually exhibit mesophases similar to those exhibited by classical calamitic liquid crystals (Yelamaggad *et al.*, 2004). Figure 1.9(b) shows an example of V-shaped mesogen.

1.3 Objectives of the research

In 1927, Vorländer reported the first liquid crystal dimers but the materials had made little impact and essentially been overlooked (Vorländer, 1927). In 1980, Kelker and Hatz made a thorough study on the known molecular building blocks and their relationships with the mesomorphic properties of such materials (Kelker and Hatz, 1980). Several dimeric liquid crystal compounds have been prepared and investigated since then, but still there are a lot to do in order to establish their structure-property relationship.

Four series of dimeric liquid crystal compounds with varieties of structural differences have been prepared. The overall objectives of the research described in this thesis are:

a) To synthesise new dimeric molecules with symmetric and non-symmetric architecture consisting of different types of mesogenic cores with variable length of flexible spacer and different terminal groups.

b) To conduct physical and spectroscopic characterisations and to study the liquid crystalline properties of these materials.

c) To investigate the structure-property relationship of these materials by increasing the flexible chain length and by varying the terminal group.

2.0 EXPERIMENTAL

2.1 Chemicals

Table 2.1. List of chemical reagents used for the syntheses

Source	Chemicals	Percentage purity (%)
Acros Organics, Belgium	Aniline	> 99
	1,6-Dibromohexane	98
	1,9-Dibromononane	97
	1,10-Dibromodecane	97
	4-Bromoaniline	99
	4-Chloroaniline	98
	4-Dimethylaminopyridine	99
	4-Ethylaniline	99
	4-Fluoroaniline	98
	4-Hydroxybenzaldehyde	99
	30% Hydrogen peroxide	-
	Dicyclohexylcarbodiimide	99
	Pentanol	99
	Potassium metabisulphide	97
	Potassium thioacetate	98
	Sulphuric acid	96
Fisher Scientific, UK	Potassium carbonate	> 99
	Potassium iodide	> 99
	Sodium hydroxide	98
R & M Chemicals, UK	Sodium iodide	> 99
Sigma Aldrich, USA	1,5-Dibromopentane	97
	1,7-Dibromoheptane	97
	1,8-Dibromooctane	98
	1,11-Dibromoundecane	98
	1,12-Dibromododecane	98
	3-Bromopropionic acid	97
	5-Bromovaleric acid	97
	6-Bromohexanoic acid	98
	8-Bromooctanoic acid	97
	10-Bromodecanoic acid	95
	11-Bromoundecanoic acid	99
	12-Bromododecanoic acid	97
	4-Iodoaniline	98
	Cholesterol	> 99
	p-Toluidine	99
	p-Toluensulfonyl chloride	> 98
Tokyo Chemical Industry, Japan	4-(4-Hydroxyphenyl)benzoic acid	> 98

2.2 Syntheses and characterisation

All compounds were synthesised, purified, recrystallised and analysed at standard atmospheric pressure 101.325 kPa.

2.2.1 Synthesis of α-{4-[(4-substituted-phenylimino)methyl]phenoxy}-ω-[4-(4-pentyloxycarbonylphenyl)phenoxy]alkanes, X-*n*-PB

The synthesis of liquid crystal dimers α-{4-[(4-substituted-phenylimino)-methyl]phenoxy}-ω-[4-(4-pentyloxycarbonylphenyl)phenoxy]alkanes, **X-*n*-PB** in which X denotes the terminal substituent while *n* denotes the nomber of carbon atoms in the flexible spacer is outlined in Figure 2.1. Condensation reaction of 4-hydroxybenzaldehyde with 4-substituted-aniline resulted in a series of Schiff bases **SB-X** (Ha *et al.*, 2009). Schiff bases **SB-X** were alkylated under classical conditions with an excess of the 1,5-dibromopentane and 1,6-dibromohexane in order to obtain the ω-brominated products **X-*n*** (Attard *et al.*, 1994). In a separate reaction, commercially available 4-(4-hydroxyphenyl)benzoic acid was reacted with pentanol in the presence of catalytic amount of concentrated sulphuric acid to obtain the ester **PB** (Yeap *et al.*, 2009). Finally, Williamson etherification reaction of compounds **X-*n*** with compound **PB** in the presence of anhydrous potassium carbonate and potassium iodide afforded the desired dimers **X-*n*-PB** (Yeap *et al.*, 2009). Intermediary compounds **X-*n*** and title compounds **X-*n*-PB** with respective terminal substituent and flexible spacer are listed in Table 2.2.

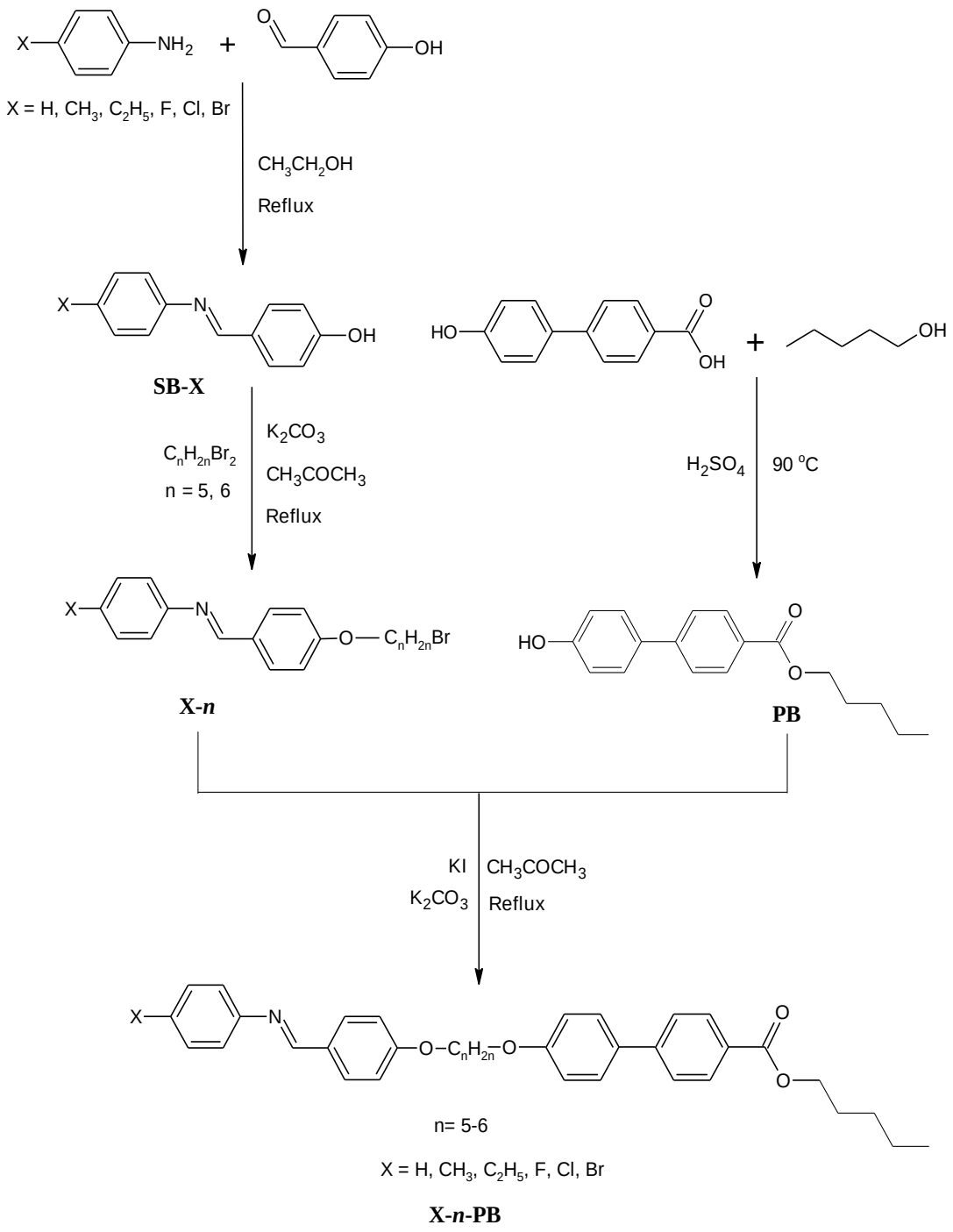


Figure 2.1. Synthetic route for the preparation of liquid crystal dimers **X-*n*-PB**

Table 2.2. Intermediary compounds **X-*n*** and title compounds **X-*n*-PB** with respective spacer (-C_nH_{2n}-) and terminal substituent (X)

Intermediate	Title compound	Terminal substituent (X)	Spacer (-C_nH_{2n}-)
H-5	**H-5-PB**	H	C_5H_{10}
CH_3-5	**CH_3-5-PB**	CH_3	C_5H_{10}
C_2H_5-5	**C_2H_5-5-PB**	C_2H_5	C_5H_{10}
F-5	**F-5-PB**	F	C_5H_{10}
Cl-5	**Cl-5-PB**	Cl	C_5H_{10}
Br-5	**Br-5-PB**	Br	C_5H_{10}
H-6	**H-6-PB**	H	C_6H_{12}
CH_3-6	**CH_3-6-PB**	CH_3	C_6H_{12}
C_2H_5-6	**C_2H_5-6-PB**	C_2H_5	C_6H_{12}
F-6	**F-6-PB**	F	C_6H_{12}
Cl-6	**Cl-6-PB**	Cl	C_6H_{12}
Br-6	**Br-6-PB**	Br	C_6H_{12}

2.2.1.1 Synthesis of 4-[(4-bromophenylimino)methyl]phenol, SB-Br

A solution of 4-bromoaniline (1.41 g, 8.2 mmol) in absolute ethanol was added dropwise to a stirring 50 mL ethanolic solution of 4-hydroxybenzaldehyde (1.00 g, 8.2 mmol) in a round-bottom flask. The reaction mixture was refluxed at 78 ^oC for 6 hours and the ethanol was left to evaporate off at room temperature. The precipitate thus obtained was recrystallised from chloroform to yield the desired Schiff base.

2.2.1.2 Synthesis of 4-[(4-substituted-phenylimino)methyl]phenols, SB-X

The same procedure described in section 2.2.1.1 was repeated to synthesise other homologues of **SB-X** using the appropriate 4-substituted-aniline in similar mole ratio.

2.2.1.3 Synthesis of 1-{4-[(4-bromophenylimino)methyl]phenoxy}-5-bromo-pentane, Br-5

A mixture containing compound **SB-Br** (0.31 g, 1.1 mmol) and anhydrous potassium carbonate (0.77 g, 5.5 mmol) was heated in 50 mL acetone. 1,5-Dibromopentane (1.77 g, 7.7 mmol) was then added dropwise into the mixture. The resulting mixture was refluxed at 56 ^{o}C for 6 hours. Upon cooling to room temperature, 40 mL water was added to the mixture. The precipitate thus obtained was filtered out and recrystallized from chloroform.

2.2.1.4 Synthesis of α-{4-[(4-substituted-phenylimino)methyl]phenoxy}-ω-bromoalkanes, X-*n*

The same procedure described in section 2.2.1.3 was repeated to synthesise other homologues of **X-5** using the respective intermediary compounds **SB-X** in similar mole ratio. Similar procedure was employed to prepare homologues of **X-6** using the same molar quantity (7.7 mmol) of 1,6-dibromohexane instead of 1,5-dibromopentane.

2.2.1.5 Synthesis of pentyl-4-(4-hydroxyphenyl)benzoate, PB

In a round-bottom flask, 4-(4-hydroxyphenyl)benzoic acid (0.50 g, 2.3 mmol) was dissolved in 40 mL pentanol. Upon addition of catalytic amount of concentrated sulphuric acid, the stirring mixture was heated at 90 ^{o}C for 20 hours. After cooling to room temperature, the excess pentanol was left to evaporate off at room temperature. The precipitate thus obtained was washed with water and then recrystallised from a mixture of hexane and chloroform in the ratio of 1:3 (v/v).

2.2.1.6 Synthesis of 1-{4-[(4-bromophenylimino)methyl]phenoxy}-5-[4-(4-pentyloxycarbonylphenyl)phenoxy]pentane, Br-5-PB

A mixture of compound **PB** (0.10 g, 0.4 mmol), anhydrous potassium carbonate (0.25 g, 1.8 mmol) and catalytic amount of potassium iodide in 50 mL acetone were heated in a round bottom flask. Subsequently, compound **Br-5** (0.15 g, 0.4 mmol) in 30 mL acetone was then added dropwise into the mixture. The stirring solution was refluxed at 56 ^{o}C for 8 hours and then cooled to room temperature. Then, 40 mL water was added to the mixture to dissolve the anhydrous potassium carbonate and potassium iodide before the precipitate was filtered off. The precipitate thus obtained was dried and recrystallised from a mixture of hexane and chloroform in the ratio of 1:3 (v/v).

2.2.1.7 Synthesis of α-{4-[(4-substituted-phenylimino)methyl]phenoxy}-ω-[4-(4-pentyloxycarbonylphenyl)phenoxy]alkanes, X-*n*-PB

The same procedure described in section 2.2.1.6 was repeated to synthesise other homologues of **X-*n*-PB** series using the respective intermediary compounds **X-*n*** in similar mole ratio.

2.2.1.8 Characterisation of intermediary and title compounds

After the synthesis and purification steps, the intermediates **SB-X**, **X-*n*** and **PB** were analysed via FT-IR and ^{1}H-NMR spectroscopic techniques. On the other hand, the title compounds **X-*n*-PB** were characterised using various techniques such as:

i. Determination of melting points using *Gallemkamp* melting-point apparatus at the School of Chemical Sciences, USM.

ii. Fourier transform infrared spectroscopy (FT-IR). The FT-IR spectra were recorded in the range of 4000-400 cm^{-1} using a Perkin Elmer 2000 FT-IR spectrophotometer on KBr discs. Analyses were done at the School of Chemical Sciences, USM.

iii. Fourier transform nuclear magnetic resonance spectroscopy (FT-NMR). For ^{1}H-NMR as well as ^{13}C-NMR, the compounds were dissolved in deuteriated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as the internal standard and then analysed using Bruker 400 MHz and 300 MHz Ultrashield^{TM} spectrometers. Analyses were performed at the School of Chemical Sciences, USM.

iv. CHN microanalyses were performed using a Perkin Elmer 2400 LS Series CHNS/O analyser at the School of Chemical Sciences, USM.

v. The liquid crystalline phase observation was performed using a Carl Zeiss Axioskop 40 polarising optical microscope equipped with a Linkam LTS350 heating stage and Linkam TMS94 temperature controller at Liquid Crystal Research Laboratory, School of Chemical Sciences, USM.

vi. The phase transition temperatures and associated enthalpies of the dimers were determined using Seiko DSC6200R differential scanning calorimeter

at Tokyo Institute of Technology, Japan. The heating and cooling rates of the Seiko DSC6200R differential scanning calorimeter are ±5 ℃min^{-1}.

2.2.2 Synthesis of α-{4-[(4-iodophenylimino)methyl]phenoxy}-ω-[4-(4-pentyloxycarbonylphenyl)phenoxy]alkanes, I-*n*-PB

The synthesis of the **I-*n*-PB** series in which *n* denotes the number of carbon atoms in the flexible spacer is outlined in Figure 2.2. 4-Hydroxybenzaldehyde was reacted with equimolar of 4-iodoaniline in ethanol under reflux. The intermediate **SB-I** obtained was then reacted with an excess amount of α,ω-dibromoalkane in acetone under reflux to yield intermediates **I-*n***. On the other hand, 4-(4-hydroxyphenylbenzoic acid) was reacted with an excess amount of pentanol together with catalytic amount of concentrated sulphuric acid to obtain the ester **PB**. The end products **I-*n*-PB** were prepared by direct alkylation of the appropriate intermediates **I-*n*** with compound **PB** in the presence of potassium carbonate and catalytic amount of potassium iodide. Intermediary compounds **I-*n*** and title compounds **I-*n*-PB** with respective flexible spacers are listed in Table 2.3.

Table 2.3. Intermediary compounds **I-*n*** and title compounds **I-*n*-PB** with respective spacer (-C_nH_{2n}-)

Intermediate	Title compound	Spacer (-C_nH_{2n}-)
I-5	**I-5-PB**	C_5H_{10}
I-6	**I-6-PB**	C_6H_{12}
I-7	**I-7-PB**	C_7H_{14}
I-8	**I-8-PB**	C_8H_{16}
I-9	**I-9-PB**	C_9H_{18}
I-10	**I-10-PB**	$C_{10}H_{20}$
I-11	**I-11-PB**	$C_{11}H_{22}$
I-12	**I-12-PB**	$C_{12}H_{24}$

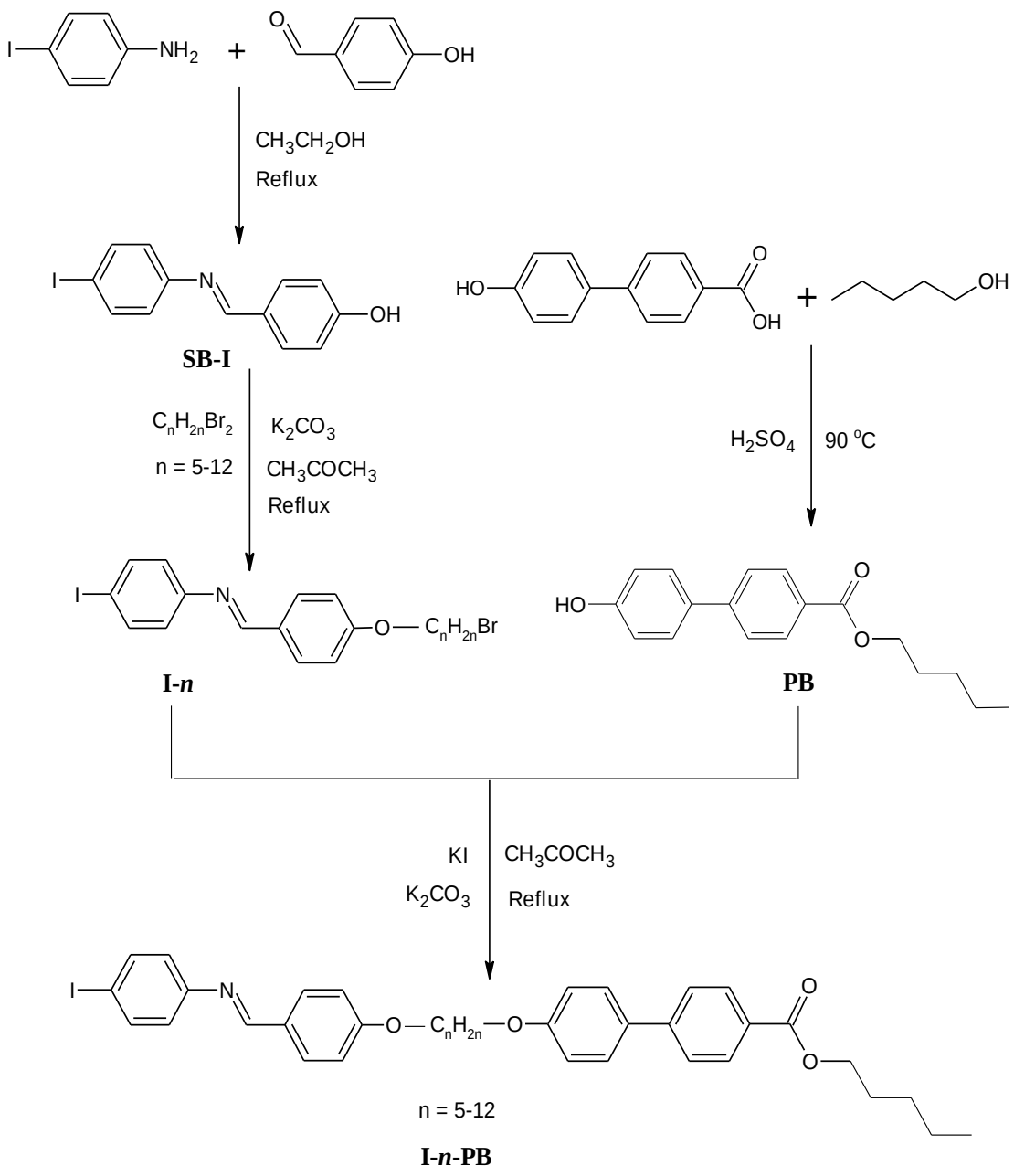


Figure 2.2. Synthetic route for the preparation of liquid crystal dimers **I-*n*-PB**